भारतीय मानक
Indian Standard

IS 1448 [P : 155] : 2020

पेट्रोलियम एवं उसके उत्पादों की परीक्षण पद्धतियाँ

[पी : 155]

रासायनिक स्फुरदीप्ति संसूचन से ऑक्सडिटिव दहन द्वारा तरल पेट्रोलियम हाइड्रोकार्बन में नाइट्रोजन का अंश ज्ञात करना

Methods of Test for Petroleum and its Products

[P : 155]

Determination of Trace Nitrogen in Liquid Petroleum Hydrocarbons by Oxidative Combustion with Chemiluminescence Detector

ICS 75.080

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Methods of Sampling and Test for Petroleum, its Products, Gaseous Fuels and Lubricants Sectional Committee, PCD 01

FOREWORD

This Indian Standard [P : 155] was adopted by the Bureau of Indian Standards after the draft finalized by the Methods of Sampling and Test for Petroleum, its Products, Gaseous Fuels and Lubricants Sectional Committee had been approved by the Petroleum, Coal and Related Products Division Council.

Determination of nitrogen in petroleum distillates is a subject of importance as presence of even trace amount of nitrogenous compounds adversely affects some process catalysts used in petroleum and chemical refining. Using this test method, the trace total nitrogen naturally found in liquid hydrocarbons can be determined.

This standard is formulated based on experience of petroleum laboratories and considerable assistance has been derived from ASTM D 4629-12 'Determination of Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection'.

Generally, the instrument for testing of nitrogen comprises injection system, horizontal furnace with combustion tube and the detector. Recently, there have been test instruments with vertical furnace, which are capable to test nitrogen as low as ppb levels. The operation and test conditions for testing is provided by the instrument manufacturers. This standard thus provides flexibility to test nitrogen in hydrocarbons at ppb levels too.

The standard covers determination of total nitrogen by two different type of instruments one with horizontal furnace or second with vertical furnace. It is experienced that instrument with vertical furnace and auto injectors have better precision than the instrument with horizontal furnace. Users can opt for either type of instrument as per the test requirement.

In reporting the results of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'.

Indian Standard

METHODS OF TEST FOR PETROLEUM AND ITS PRODUCTS

[P : 155]

DETERMINATION OF TRACE NITROGEN IN LIQUID PETROLEUM HYDROCARBONS BY OXIDATIVE COMBUSTION WITH CHEMILUMINESCENCE DETECTOR

1 SCOPE

1.1 This standard [P : 155] describes the procedure for measuring total trace nitrogen naturally found in liquid hydrocarbons (boiling range from approximately 50 to 400°C), with viscosities between approximately 0.2 and 10 cSt at room temperature.

1.2 This method is not applicable to diatomic nitrogen (N_2) and has reduced sensitivity to compounds with nitrogen-nitrogen bonds that decompose to produce nitrogen gas.

NOTES:

1 Instruments with horizontal furnace can determine the total trace nitrogen in naphtha, distillates and oils containing 0.3 to 100 mg/kg total nitrogen. Instruments with vertical furnace and auto injector are capable for determination of nitrogen in liquid hydrocarbons at concentrations ranging from 50 to 300 ng/g (mass in ppb). It is also applicable to highly volatile samples such as pentane through the use of cooled sampling system.

2 This test method can be applied to sample types outside the range of the scope by dilution of the sample in an appropriate solvent to bring the total nitrogen concentration to within the range covered by the test method. However, it is the responsibility of the analyst to verify the solubility of the sample in the solvent.

2 REFERENCES

The following standards contain provisions, which, through reference in this text, constitute provisions of the standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below:

IS No.	*Title*
1448	Methods of test for petroleum and its products
[P : 16] : 2014/ ISO 3675 : 1998	Density, relative density or API gravity of crude petroleum and liquid petroleum products by hydrometer method (*third revision*)
[P : 32] : 1992	Density and relative density (*second revision*)

3 PRINCIPLE

The liquid hydrocarbon is injected into a stream of inert gas (argon or helium). The liquid is vapourized inside horizontal or vertical type of furnace based on the design of instrument and carried to a high temperature zone where it is mixed with oxygen, organically bonded nitrogen is converted to nitric oxide. The nitric oxide reacts with ozone and is converted into excited nitrogen dioxide. A photomultiplier tube detects the light emitted as the excited nitrogen dioxide decays and the resulting signal is a measure of nitrogen contained in the liquid hydrocarbon.

4 SIGNIFICANCE

Many of the process catalyst, used in petroleum refining are poisoned due to trace amounts of nitrogenous compounds present in the feedstocks. The standard can essentially measure bonded nitrogen in process feeds and can be used for controlling nitrogen compounds in finished products.

5 APPARATUS

NOTE — Requirement of accessories for apparatus may slightly differ for instruments from different manufacturers. However, for such selection, recommendation of the instrument manufacturer shall be followed.

5.1 Furnace (Electric)

Based on the design of the instrument, either a horizontal furnace or vertical furnace may be used. The furnace is operated at a temperature sufficient to volatilize and pyrolyze the entire sample and oxidize the organically bound nitrogen; typical furnace temperature may be around 1 000°C or as recommended by the manufacturer.

5.2 Combustion Tube

Fabricated to meet the instrument manufacturer’s specifications.

5.3 Drier Tube

Since, the reaction products include water vapour, it is necessary to eliminate before it reaches the detector. This is achieved with the use of a magnesium perchlorate [Mg $(ClO_4)_2$] scrubber or a membrane drying tube (permeation drier) or as recommended by instrument manufacturer.

5.4 Chemiluminescent Detector

Capable of measuring light emitted from the reaction between nitric oxide (NO) and ozone.

5.5 Totalizer

With variable attenuation and capable of measuring, amplifying, and integrating the current from the chemiluminescence detector. A built in microprocessor or attached computer system may perform these functions.

5.6 Micro-litre Syringe

Capacity of 5, 10, 25, 50, 100 or 250 µl, with needle that is long enough to reach the hottest portion of inlet section of the furnace when injecting the sample. The syringe may be part of an automatic sampling and injection device used with the instrument.

5.7 Recorder

5.8 Sample Inlet System

Either of the following can be used:

5.8.1 *Manual Sample Injection with Syringe*

Auto sampler having a yringe and constant rate injector system, capable for injecting precise amount of sample with controlled rate.

5.8.2 *Boat Inlet System*

To facilitate analysis of samples that would react with the syringe or syringe needle. The pyrolysis tube for boat inlet use may require specific construction to permit insertion of a boat fully into the inlet section of the furnace. The boat inlet system external to the furnace shall be cooled to a temperature below room temperature to aid in dissipating the heat from the boat when it is removed from the furnace. Cooling the boat inlet system may also reduce the chances of the sample combusting in the boat before introducing into the furnace and may be necessary when running volatile samples such as naphtha using a boat inlet system.

5.9 Quartz Insert Tube

Quartz insert tube with an oxidation catalyst, as recommended by the instrument manufacturer that aids in complete oxidation. Generally cupric oxide may be used as oxidation catalyst. This is inserted into the exit end of the pyrolysis tube.

5.10 Vacuum System

The chemiluminescence detector may be equipped with a vacuum system to maintain the reaction cell at reduced pressure (typically 20 to 25 mm Hg). This can improve the signal to noise ratio of the detector.

NOTE — It is observed that instruments that uses vacuum system gives better precision and accurate results.

5.11 Analytical Balance — With a precision of ± 0.01 mg.

6 REAGENTS

6.1 Follow Material Safety Data Sheet (MSDS) of reagents for safety precautions.

NOTES:

1 Requirement of reagents and chemicals may slightly differ for instruments from different manufacturers. However, for such selection, recommendation of the instrument manufacturer shall be followed.

2 High temperature is employed in this test method. Since the instrument is operated at high temperature, exercise care when using flammable materials near the pyrolysis furnace.

6.2 Quality of Reagents

Unless specified otherwise, only “Analytical Grade” chemicals shall be used for testing. It need to be ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination

NOTE — ‘Pure chemicals’ shall mean chemicals that do not contain impurities which affect the results of analysis.

6.3 Magnesium Perchlorate, Mg $(ClO_4)_2$ — For drying products of combustion (if permeation drier is not used.)

6.4 Inert Gas — Helium or argon (ultra high pure).

6.5 Oxygen — 99.996 percent minimum pure.

6.6 Solvents — For dilution and matrix matching such as, toluene, isooctane, xylene, acetone, cetane. (Other solvents similar to those occurring in samples can also be used). Solvents should contain less than 0.1 µg/ml nitrogen. For samples with less than 300 ng/ml nitrogen, solvents with less than 30 ng/ml shall be used.

6.7 Nitrogen Stock Solution (1 000 µg N/ml)

Stock solution is prepared by accurately weighing 1.195 g of carbazole or 0.565 g of pyridine, into a tared 100 ml volumetric flask. 15 ml of acetone is then added while using carbazole to dissolve it. Dilute to volume with the selected solvent. Calculate the exact concentration of the stock solution based on the actual mass of pyridine or carbazole and the purity of the chemical used. This stock is further diluted to desired nitrogen concentrations.

NOTES:

1 Pyridine is used with low boiling solvents (boiling point <220°C) and carbazole with high boiling solvents (boiling point >220°C).

2 Working standards are to be remixed on a regular basis depending upon frequency of use and age. Typically, working standards have a useful life of about 3 months, and are refrigerated when not being used.

6.8 Cupric Oxide Wire — As recommended by instrument manufacturer.

6.9 Quartz Wool

6.10 Pyridine

6.11 Carbazole

7 APPARATUS ASSEMBLY

7.1 Install the apparatus as provided in the manufacturer's manual.

7.2 Set the flow of various gases and the pyrolysis temperature as recommended by the instrument manufacturer.

8 CALIBRATION AND STANDARDIZATION

8.1 Prepare various calibration standards using 1 000 **µg** N/ml stock solution covering the required range of analysis and consisting matrix similar to that of sample to be tested. Generate calibration curve using atleast two calibration standards in addition to the solvent blank.

8.2 Determine volume or mass of the material to be analyzed by using either of the volumetric or gravimetric method described below.

8.2.1 Volumetric measurement of the injected material is obtained by filling the syringe to the 80 percent level, retracting the plunger so that the lower liquid meniscus falls on the 10 percent scale mark, and recording the volume of liquid in the syringe. After the material was injected, again retract the plunger so that the lower liquid meniscus falls on the 10 percent scale mark and record the volume of liquid in the syringe. The difference between the two volume readings is the volume of material injected.

8.2.2 Alternatively, an automatic sampling and injection device may be used to inject a reproducible volume of the material into the furnace.

8.2.3 Gravimetric measurement of the injected material is obtained by weighing the syringe before and after injection to determine the quantity of material injected. The gravimetric procedure provide better precision than the volumetric procedure, when a balance with a precision of at least ± 0.01 mg is used.

8.3 For injecting the sample into the furnace, insert syringe needle through the inlet septum up to the syringe barrel and inject the sample or standard at a uniform rate as specified by the instrument manufacturer (generally 0.2 to 1.0 µl/s). Rate of injection of sample is based on factors such as viscosity, hydrocarbon type and nitrogen concentration. The user must ensure a method whereby sample is injected with consistent and uniform rate of injection. An automatic sampling and injection device may be used at a reproducible rate of injection.

NOTES:

1 For the most consistent injection rate and best analytical results, a constant rate injection unit or automatic sampling and injection device may be helpful. Coke formation at the outlet of the combustion tube may indicate too rapid of an injection rate. Consult manufacturer for recommendations.

2 In case of, direct injection below 5 mg/kg of nitrogen, the needle septum blank is increasingly important. Error due to this can be avoided by inserting the syringe needle into the hot inlet and allowing the needle-septum blank to dissipate before injecting the sample.

8.4 If a boat inlet system is used, then the material to be analyzed is injected into a quartz boat using one of the procedures described in **8.2** and the quartz boat is moved into the hot portion of the combustion tube. Details of operation as available in manufacturer's manual may be referred.

8.5 Calibration curve shall be generated in one of the following manners depending on the capability of the instrument used.

8.5.1 For systems that use a microprocessor or computer system for data collection and calibration curve generation, calibration curve shall be based on the linear regression minimum of three repeat measurements of each calibration standard.

8.5.2 For those detectors not equipped with a microprocessor or computer system for generating a calibration curve, construct a standard curve as follows:

a) Repeat the determination of each calibration standard and the blank three times.
b) Determine the average net response of each.
c) Construct a curve plot of detector response (integration counts) versus nanograms of nitrogen injected and apply the best straight line fit through the plotted data.

8.6 The response curve should be linear with a minimum R^2 of 0.999. The intercept should not be forced through zero. The calibration curve shall be checked each day that instrument is used.

8.7 Quality Control

Once in a month, run a blank (diluents mixture) and any mid-range internal standard on the prepared calibration line. The observed results shall remain within the precision of this method. In case large deviations are observed or desired precision is not met, recalibrate the instrument again.

9 PROCEDURE

NOTE — Volatile samples should be kept in airtight containers and should be analyzed as soon as possible so as to prevent reduction of nitrogen or contamination due to exposure or contact with sample container.

9.1 Concentration of nitrogen in the test specimen must be less than the concentration of the highest standard used in the calibration. Injection volumes may vary from 3 to 100 µl depending on the instrument being used and shall be similar to the size of the injected standards used for calibration.

9.2 Flush a clean syringe several times with the sample to be tested. Inject it into the furnace using the procedure outlined in **8.2** to **8.4.** For samples with total concentration of nitrogen in the range 1 to 100 mg/kg, quantity of sample injected is typically up to 10 µl. For samples with total concentration of nitrogen less than 1 mg/kg, injected sample can be up to 100 µl. Follow the manufacturer's manual on sample size based on type of sample and level of nitrogen present.

9.3 To obtain one result, measure each test specimen a minimum of three times and calculate the average detector response.

10 CALCULATION

10.1 For samples introduced volumetrically, density values at ambient temperature shall be used for calculation.

10.2 Calculate the nitrogen content of the sample in mg/kg for the average of the three determinations that make up a single result as follows:

$$\text{Nitrogen, mg/kg} = \frac{(I - I_0) \times K}{(S \times V \times D)} \tag{1}$$

or

$$\text{Nitrogen, mg/kg} = \frac{(I - I_0) \times K}{(S \times M)} \tag{2}$$

Where,

D = density of sample, g/ml;

S = slope of the calibration curve, counts/ng N;

V = volume of sample, µl;

K = dilution factor;

M = mass of sample, mg;

I = average detector response, integration counts; and

I_0 = intercept of the calibration curve, integration counts.

10.3 For analyzers equipped with a calibration adjust, calculate the nitrogen content of the sample in mg/kg as follows (the average of three determinations makes up a single result):

$$\text{Nitrogen, mg/kg} = \frac{(I - B) \times K}{(V \times D)} \tag{3}$$

or

$$\text{Nitrogen, mg/kg} = \frac{(I - B) \times K}{(M)} \tag{4}$$

where,

D = density of sample, g/ml,

V = volume of sample, µL,

K = dilution factor,

M = mass of sample, mg,

I = visual display reading of the sample, ng N; and

B = average of visual display readings of the blank, ng N.

11 REPORT

For results equal to or greater than 1 mg/kg, report the nitrogen result to two significant figures when two or more significant figures are available. For results less than 1 mg/kg, report the nitrogen result to the nearest tenth of an mg/kg.

12 PRECISION AND BIAS

12.1 The precision of this test method as determined by statistical examination of inter laboratory results is as follows (*see* Table 1).

12.1.1 *Repeatability*

The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in only one case in twenty, where X = the average of the two test results.

$$r = 0.1825(X)^{0.5149}$$

12.1.2 *Reproducibility*

The difference between two single and independent test results obtained by the different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in only one case in twenty, where X = the average of the two test results.

$$R = 0.8094(X)^{0.5149}$$

12.2 The bias of this test method cannot be determined since an appropriate standard reference material containing a known trace level of nitrogen in a liquid petroleum hydrocarbon is not available to form the basis of a bias study.

Table 1 Repeatability and Reproducibility

(*Clause* 12.1)

Sl No.	**Concentration (mg/kg N)**	***r***	***R***
(1)	(2)	(3)	(4)
i)	100	2.0	8.7
ii)	75	1.7	7.5
iii)	50	1.4	6.1
iv)	25	1.0	4.2
v)	10	0.6	2.6
vi)	1	0.18	0.81
vii)	0.3	0.10	0.44

12.3 Precision data for levels below 300 mg/g N shall be taken from the instrument manufacturer based on requirements.

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Amendments are issued to standards as the need arises on the basis of comments. Standards are also reviewed periodically; a standard along with amendments is reaffirmed when such review indicates that no changes are needed; if the review indicates that changes are needed, it is taken up for revision. Users of Indian Standards should ascertain that they are in possession of the latest amendments or edition by referring to the latest issue of 'BIS Catalogue' and 'Standards: Monthly Additions'.

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